

Degradation of PEMFC at low loadings

P. Gazdzicki, J. Mitzel, A. Dreizler, M. Schulze, K.A. Friedrich

German Aerospace Center (DLR), Institute of Engineering Thermodynamics,
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

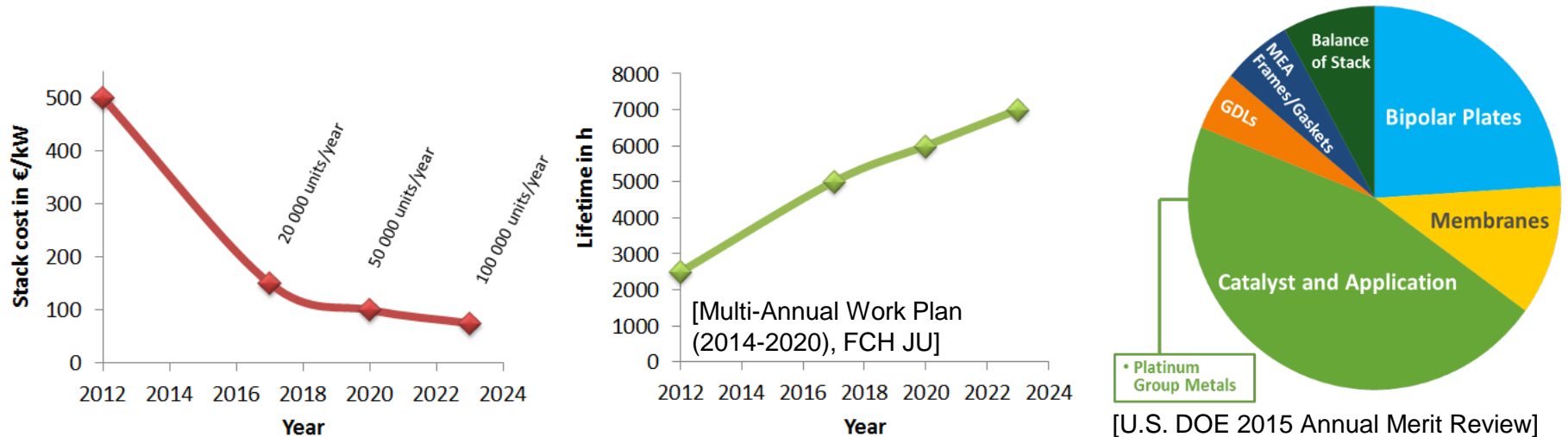
Contents

- **Motivation**
- **Irreversible Degradation**
- **Reversible Degradation**
- **Performance vs Pt-loading**
- **Degradation vs Pt-loading**
- **Summary**



Requirements for PEMFC development

- Reduction of manufacturing cost at increased durability in order to compete with conventional technologies



- Most promising regarding cost reduction: catalyst layer (45 % of stack cost)
 - **Low loadings**
 - Alternative catalysts



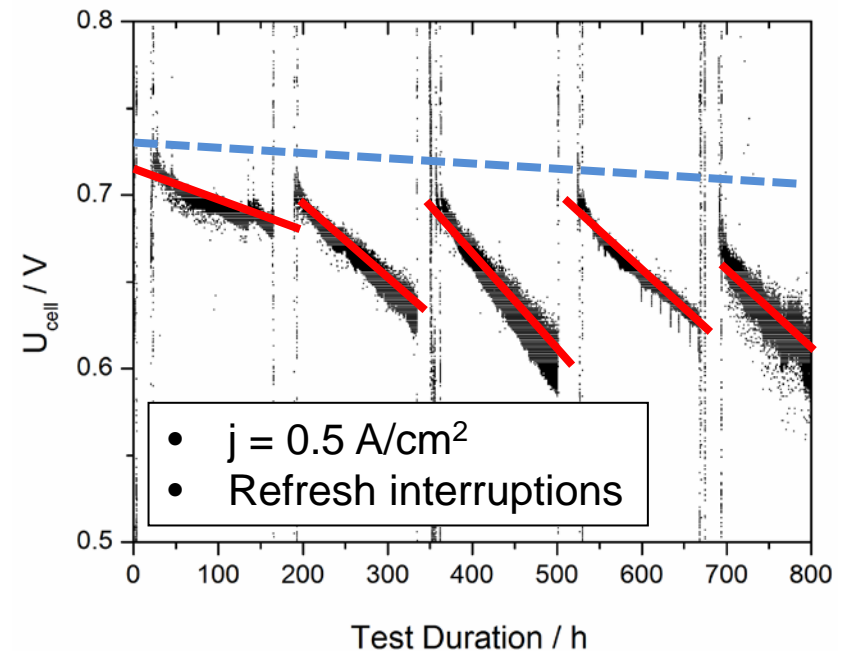
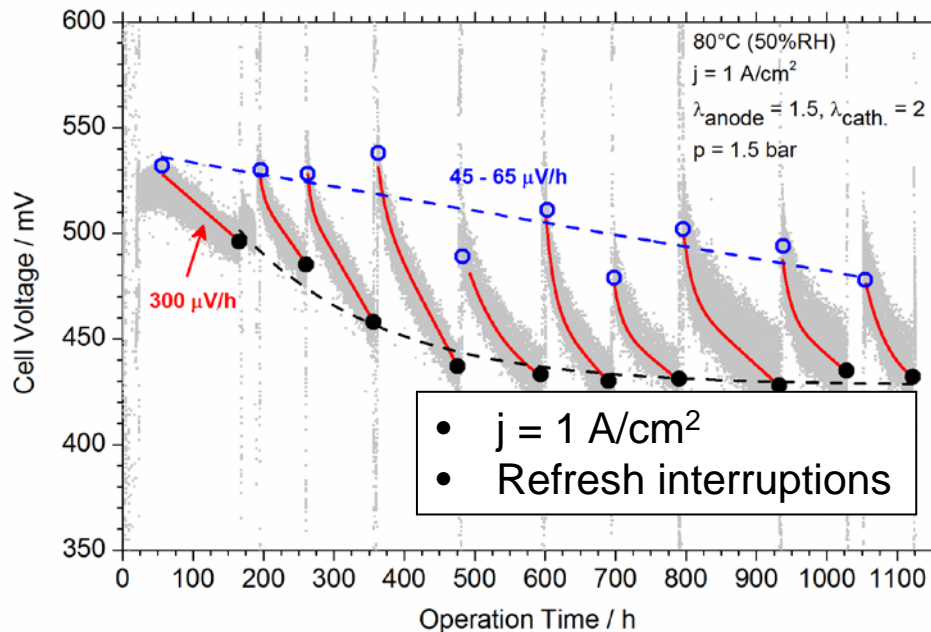
Motivation

Performance targets clearly defined and well verifiable, BUT

determination of **degradation rates** is not well defined.

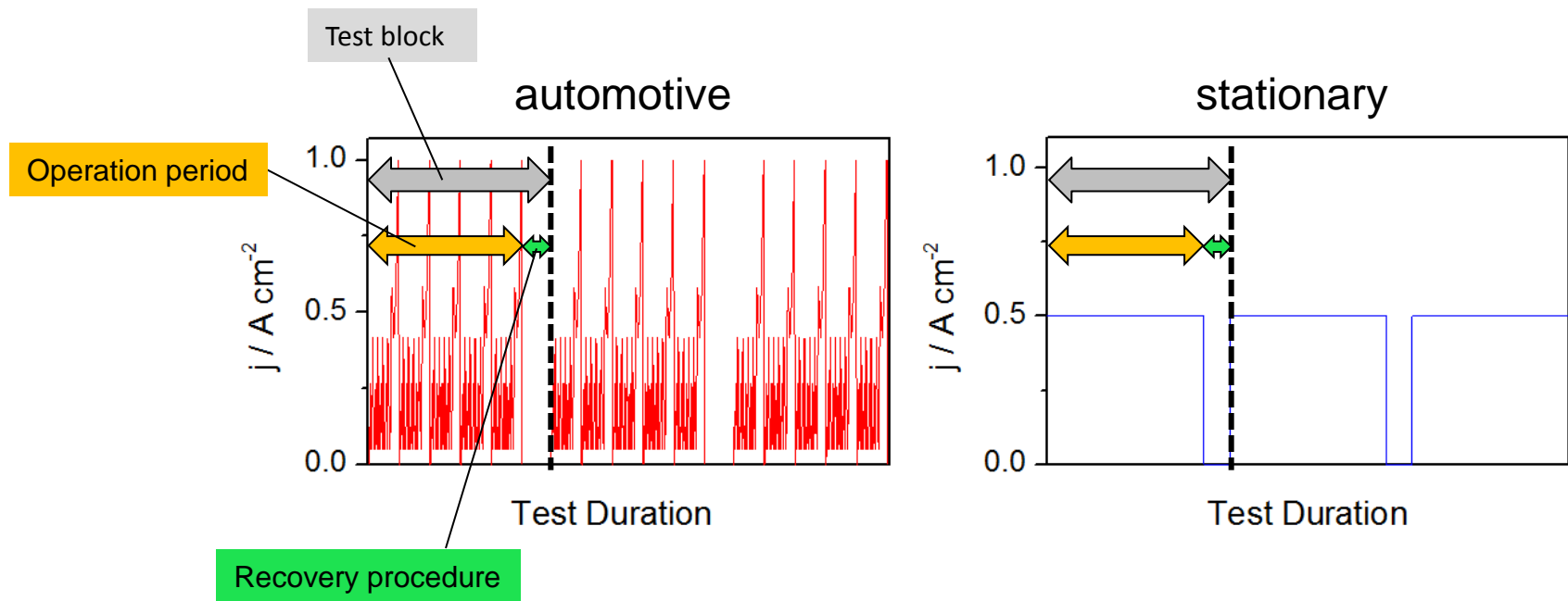
→ How to determine if **durability goals** are achieved?

Discrimination between **reversible** and **irreversible** degradation needed



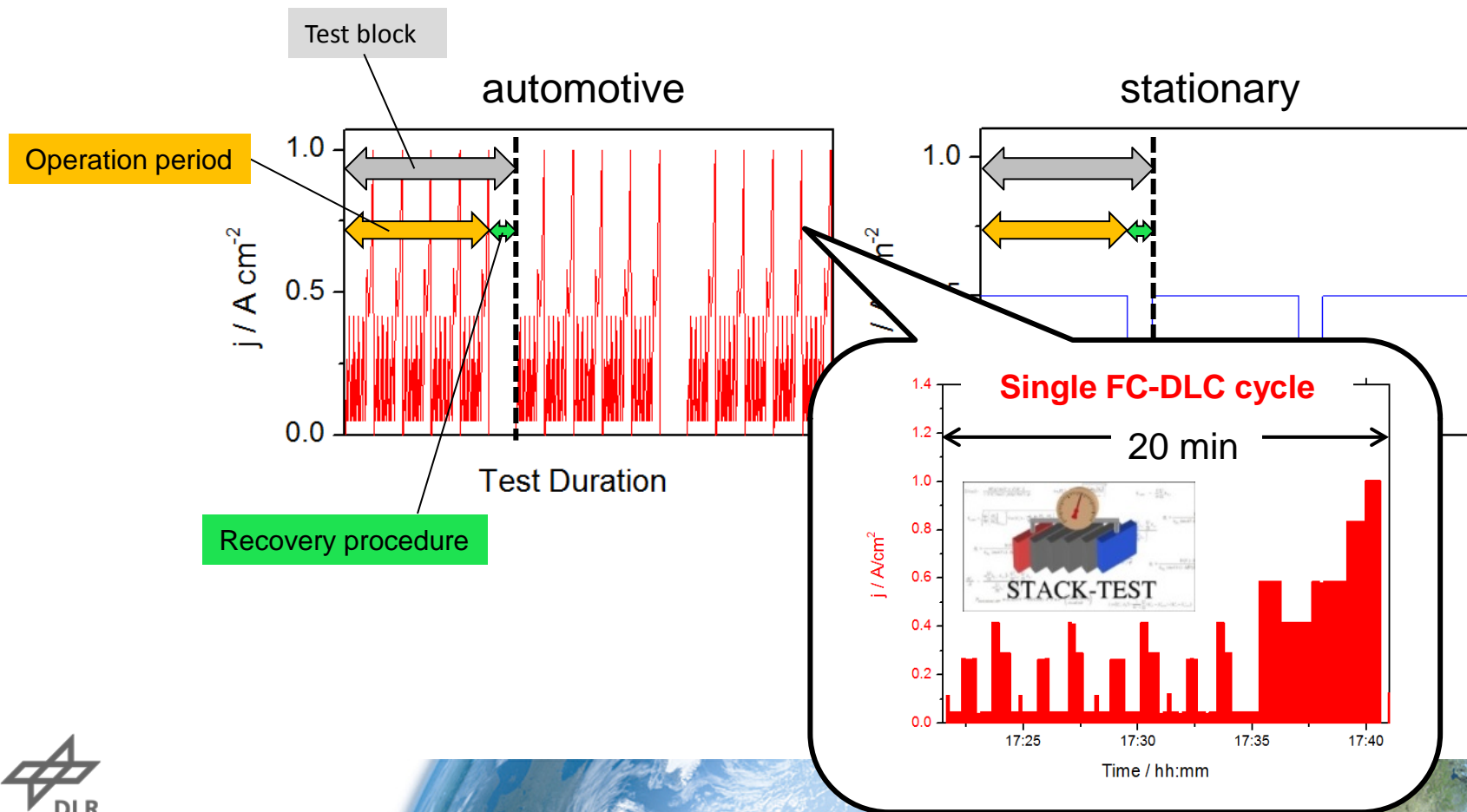
Evaluation of irreversible degradation

Durability tests consist of several test blocks of an **operation period** and a **recovery procedure**



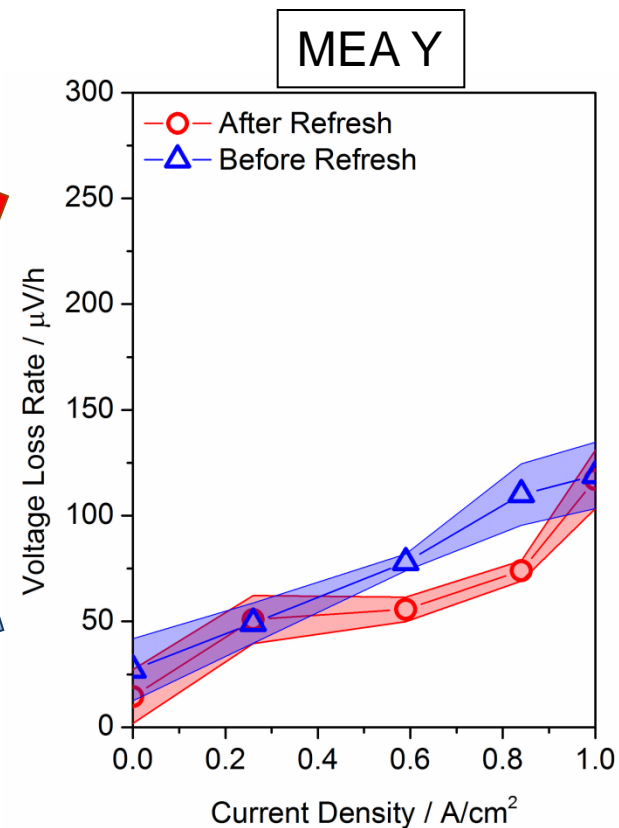
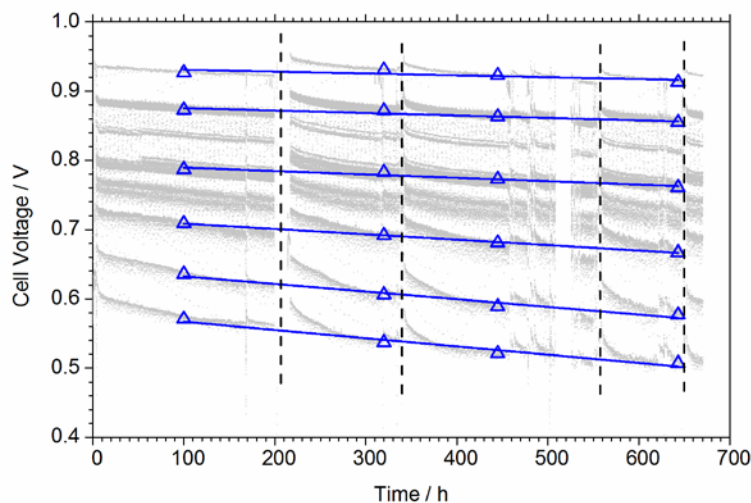
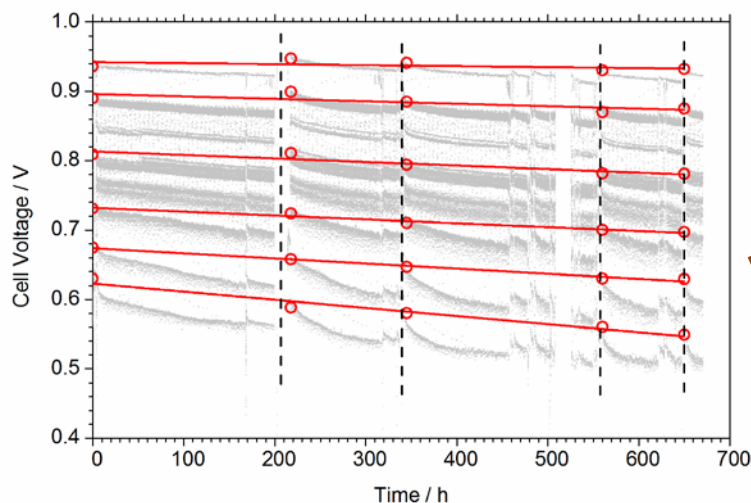
Evaluation of irreversible degradation

Durability tests consist of several test blocks of an **operation period** and a **recovery procedure**

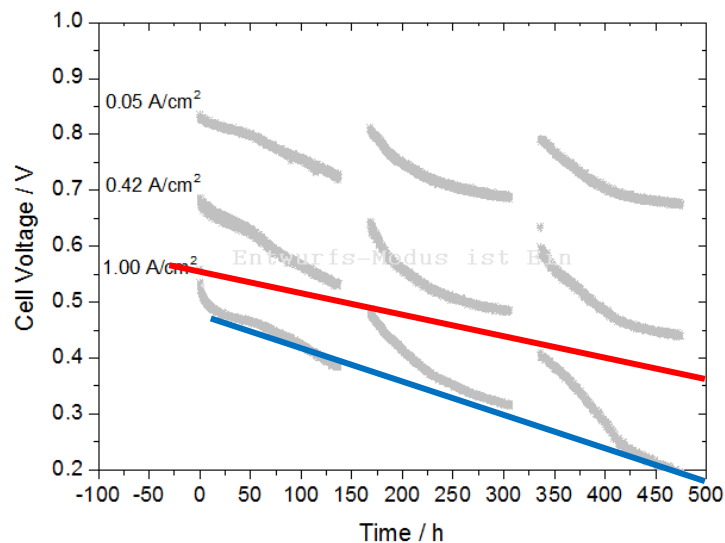


Evaluation of irreversible degradation

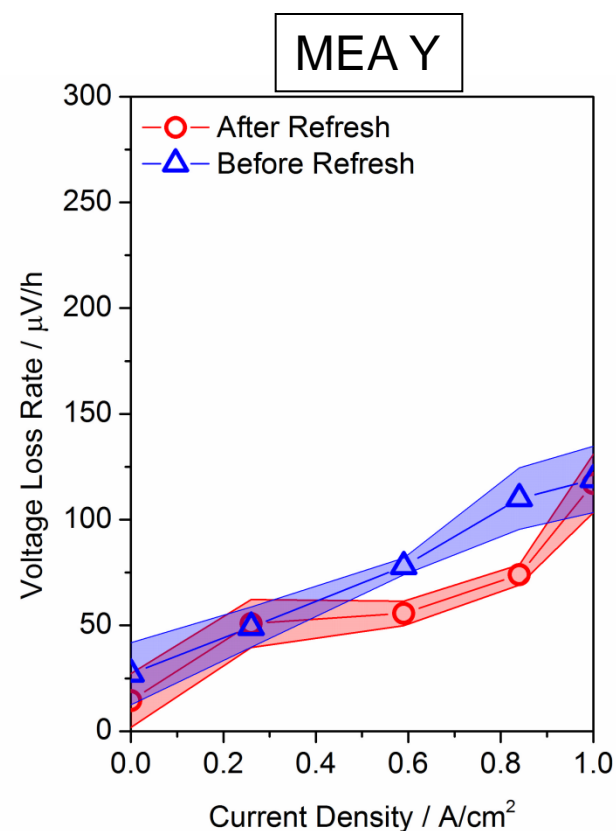
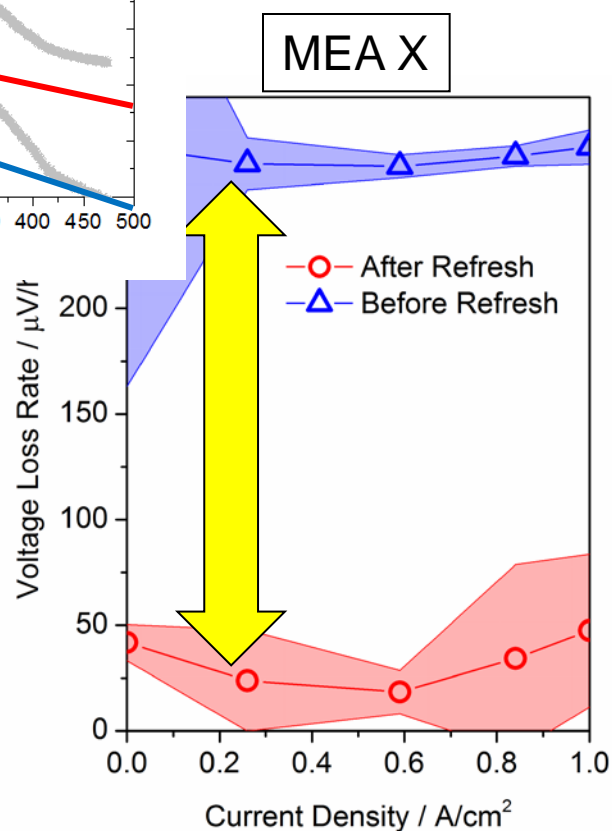
Use voltage values before or after refresh?



Evaluation of irreversible degradation



Use voltage values before or after refresh?

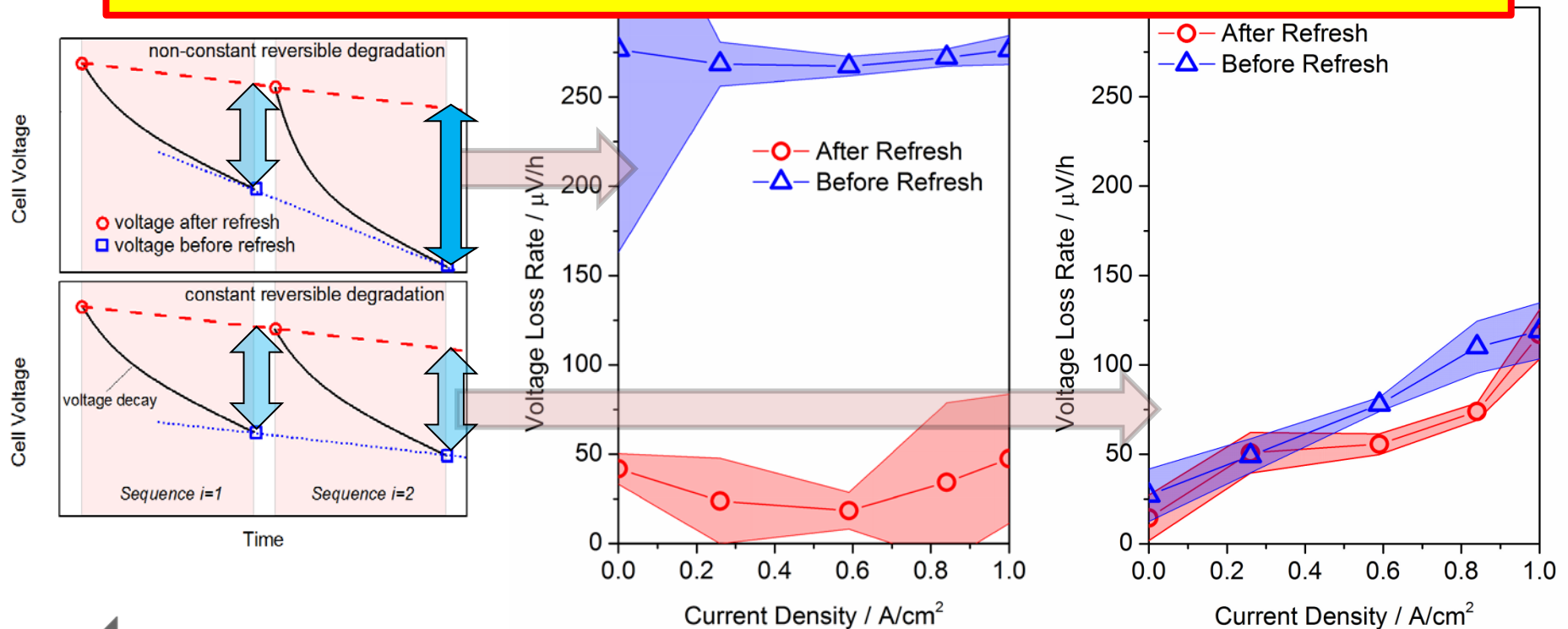


Evaluation of irreversible degradation

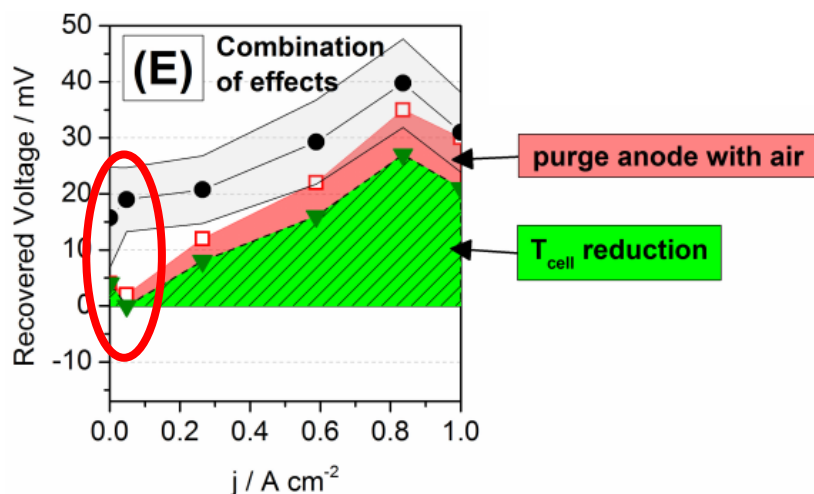
Constant and non-constant reversible degradation

→ decay rate(...): combination of **reversible** and **irreversible** degradation

→ decay rate(---): **irreversible** degradation



Recovery of reversible degradation

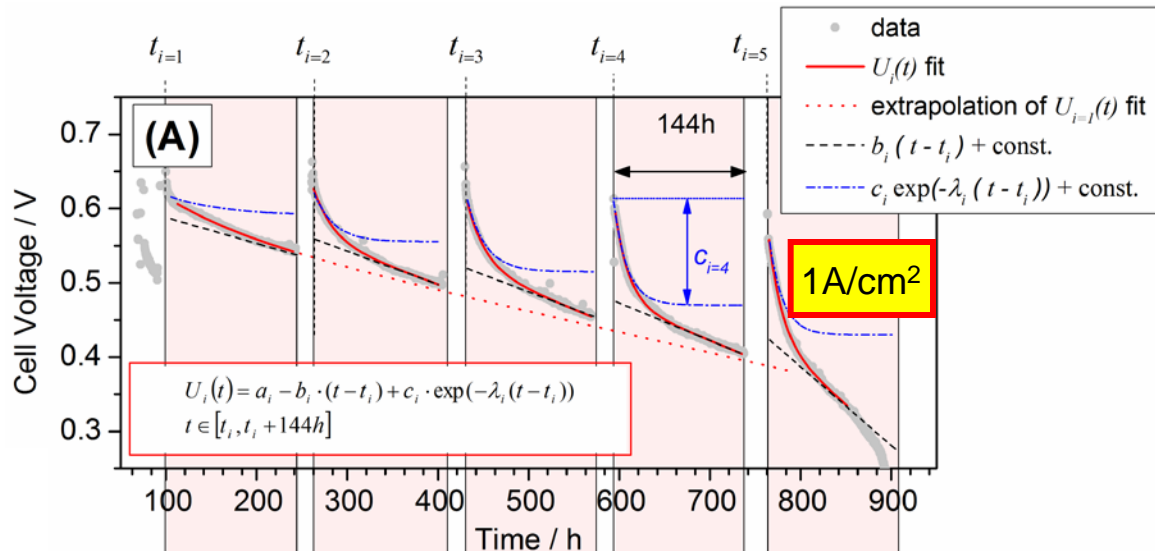


| Recovery test | Intention | Recovered voltage @ 0.2 A cm^{-2} | Recovered voltage @ 0.8 A cm^{-2} |
|-------------------------------------|---|---|---|
| Purging anode with dry H_2 | Remove water from anode | -28 % | -20 % |
| Purging cathode with dry air | Remove water from cathode | 19 % | -10 % |
| Reduction of cell temperature | Increase humidity and decrease mechanical membrane stress | 38 % | 68 % |
| OCV-Test | Drying of MEA and increase of cathode potential | 0 % | 0 % |
| Purging anode with air | Increase anode potential to remove contaminants | 19 % | 20 % |
| Stopping gas flow | Increase anode potential to remove contaminants | 0 % | 10 % |
| Purging cathode with N_2 | Decrease cathode potential to reduce platinum oxide | 14 % | 21 % |

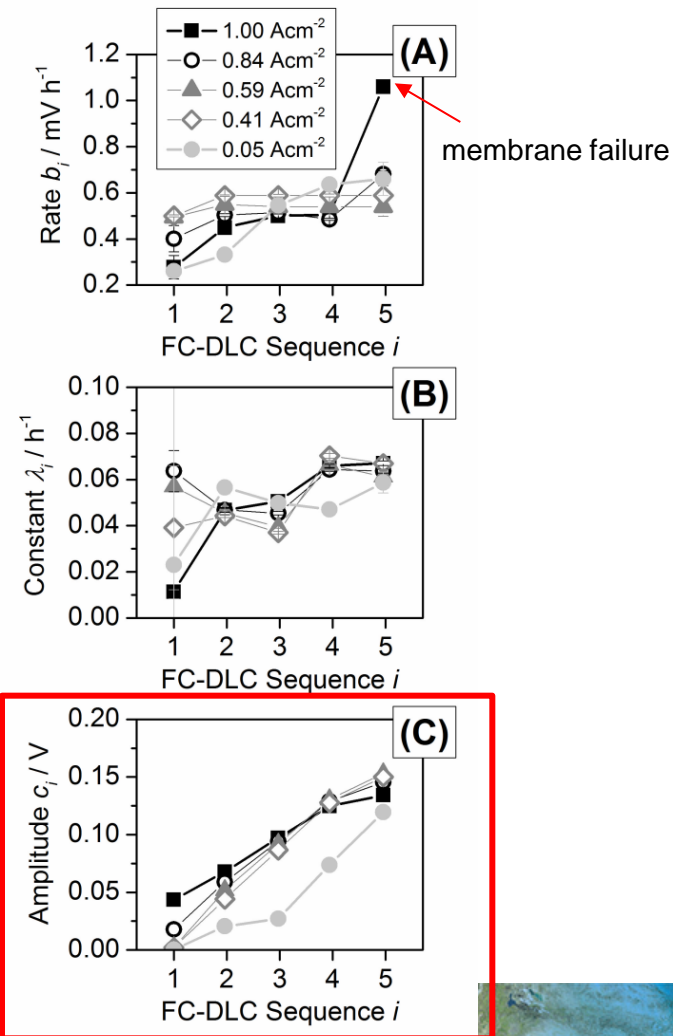
- Water management plays major role in recovery
- Reason for recovery at low loads unclear

Evaluation of reversible degradation

Mathematical description of reversible degradation



Amplitude of exp. part responsible for increase of reversible degradation with operation time



Pt-Loading Rainbow Stack Study

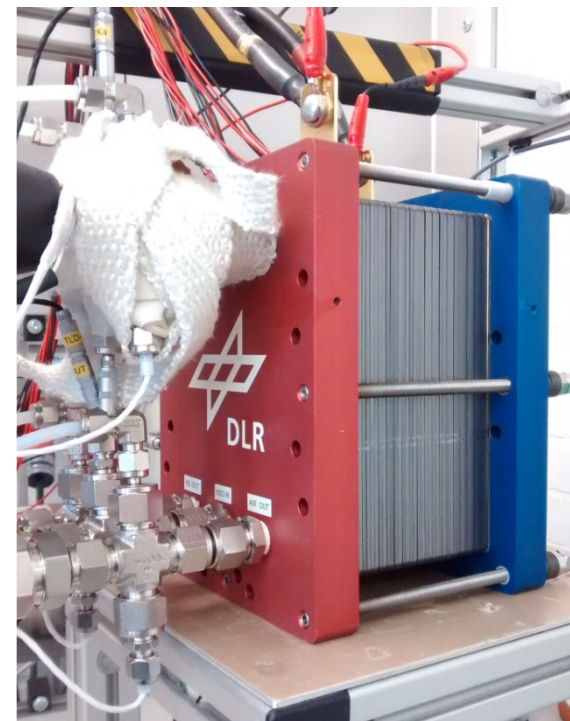
Pt-loadings at anode/cathode in $\text{mg}_{\text{Pt}}/\text{cm}^2$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---------|---------|---------|-----------|-----------|-----------|-----------|-----------|-----------|---------|-----------|-----------|-----------|-----------|-----------|-----------|---------|---------|---------|
| MEA0476 | MEA0476 | MEA0476 | 0.05/0.20 | 0.05/0.30 | 0.05/0.40 | 0.05/0.15 | 0.10/0.40 | 0.20/0.40 | MEA0476 | 0.05/0.20 | 0.05/0.30 | 0.05/0.40 | 0.05/0.15 | 0.10/0.40 | 0.20/0.40 | MEA0476 | MEA0476 | MEA0476 |

Different Pt loadings

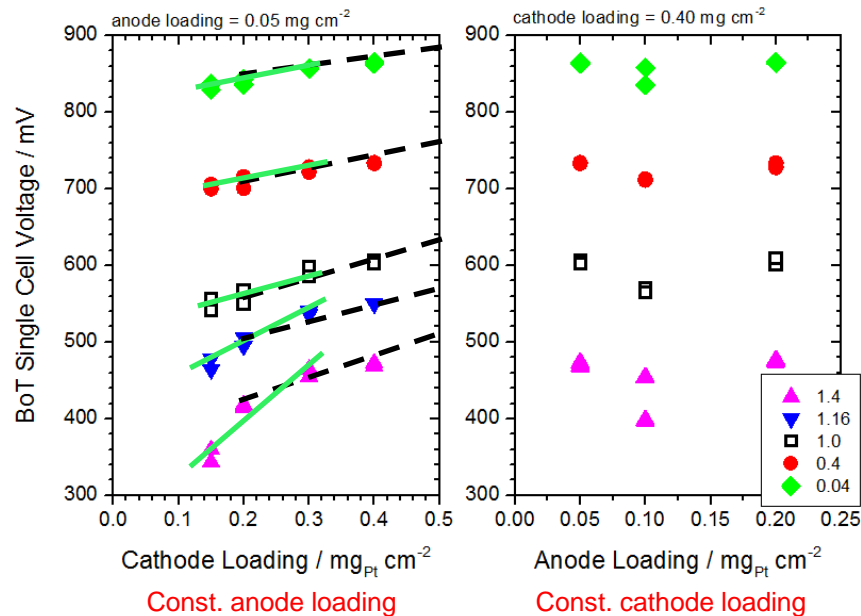
Different Pt loadings

DLR Rainbow-Stack



Performance Vs Pt-loading

BoT Voltages versus Loading

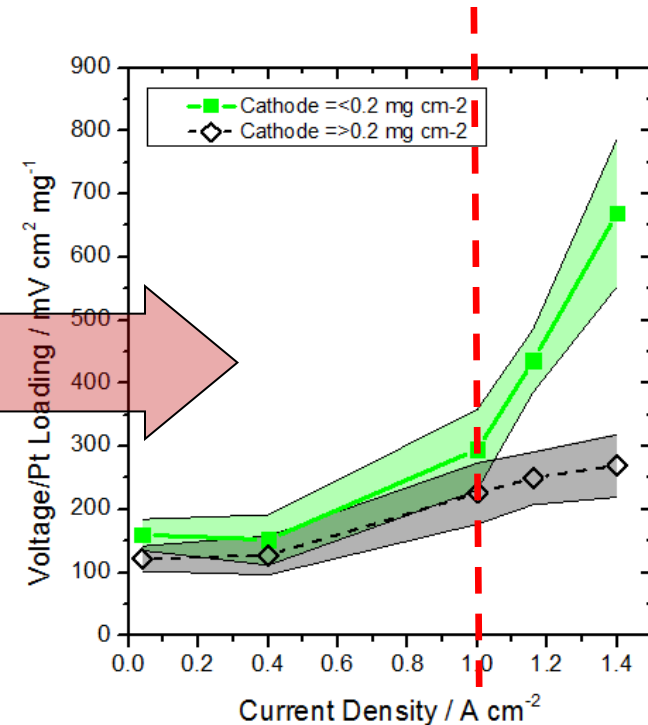
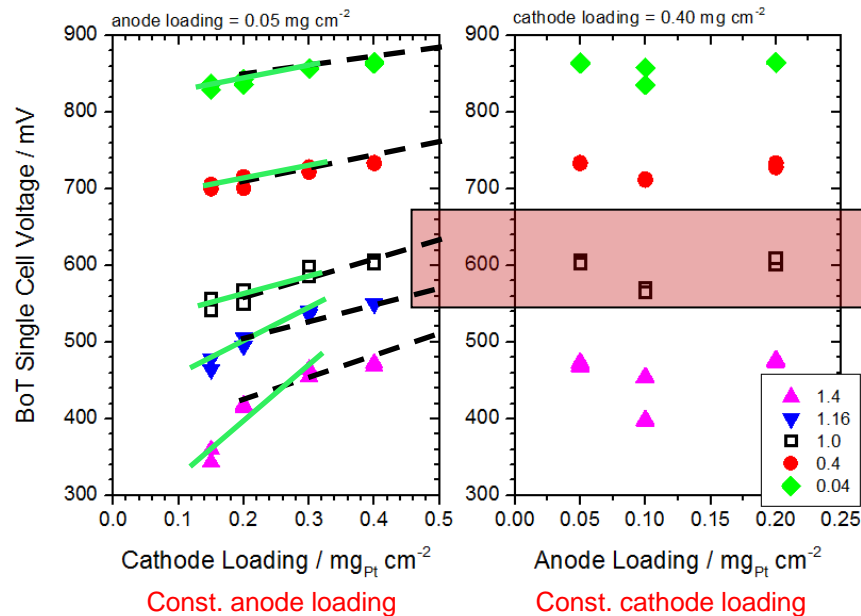


- Clear dependence of Cell Voltage on cathode Pt loading
- No dependence of Cell Voltage on anode Pt loading



Performance Vs Pt-loading

BoT Voltages versus Loading

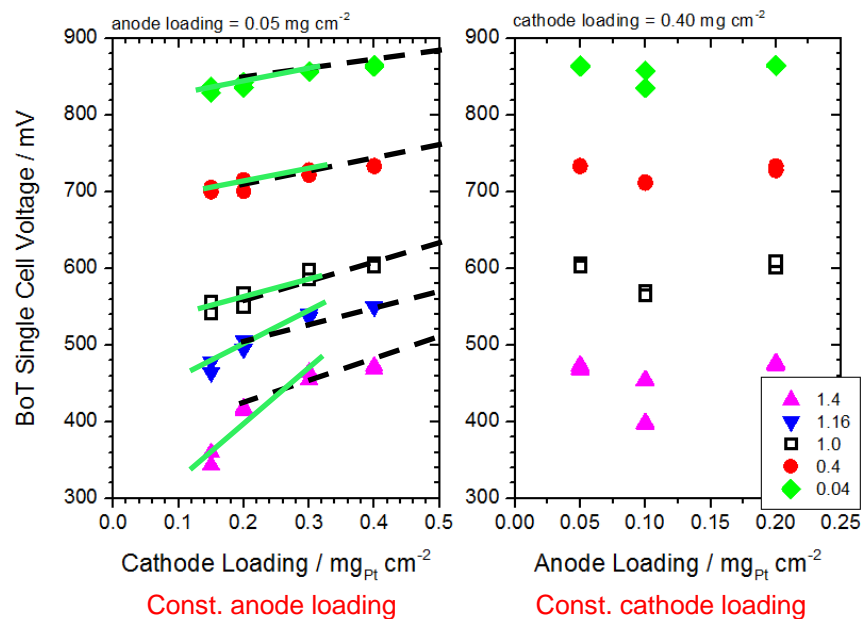


- Clear dependence of Cell Voltage on cathode Pt loading
- No dependence of Cell Voltage on anode Pt loading
- Onset of mass transport issues observed at cathode loading ≤ 0.2 mg/cm² and j > 1 A/cm²

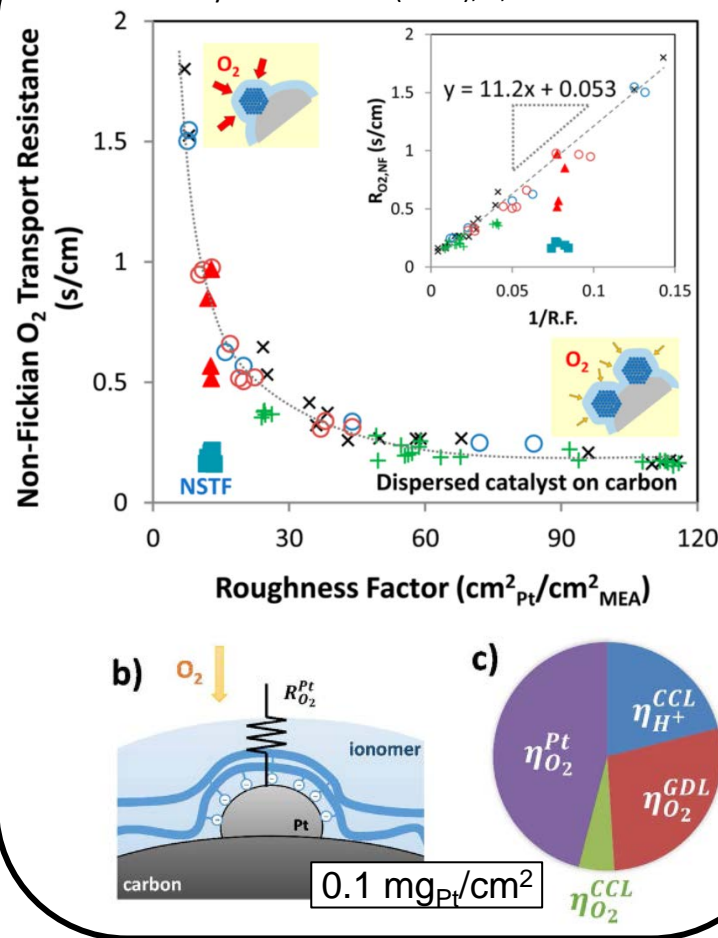


Performance Vs Pt-loading

BoT Voltages versus Loading



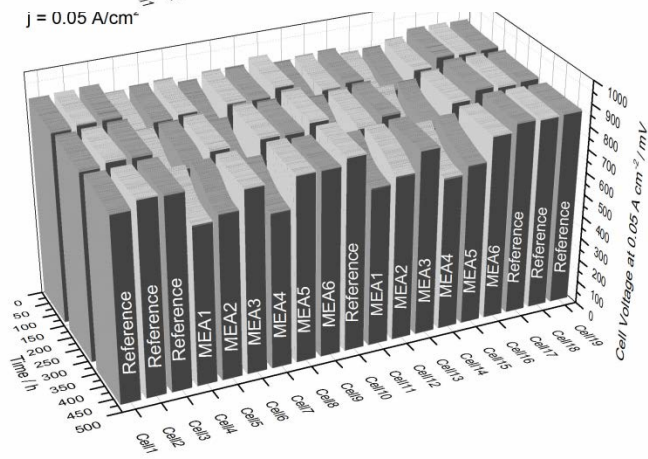
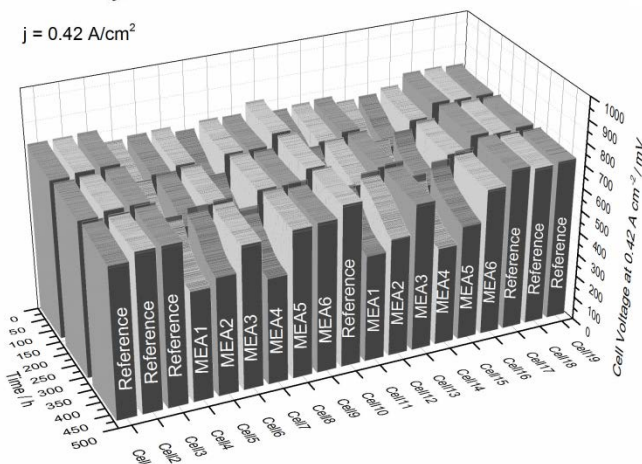
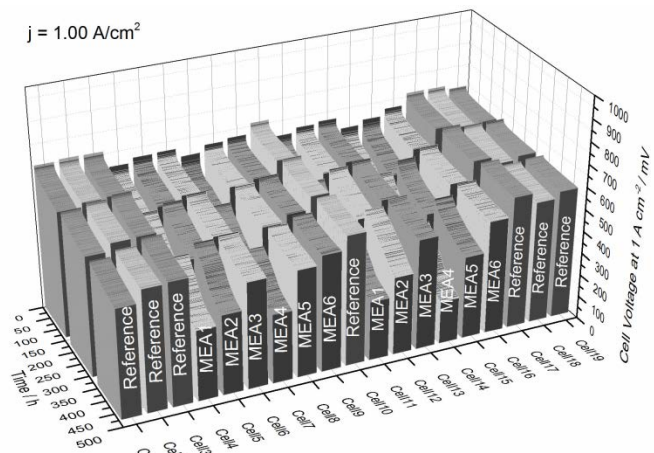
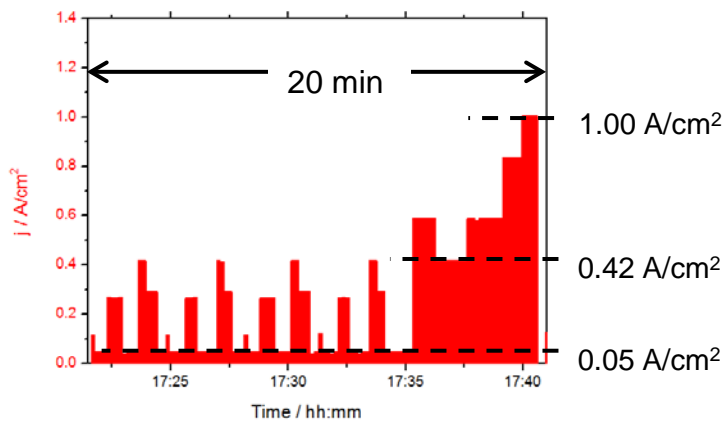
SOURCE: A. Kongkand and M.F. Mathias, J. Phys. Chem. Lett. (2016), 7, 1127



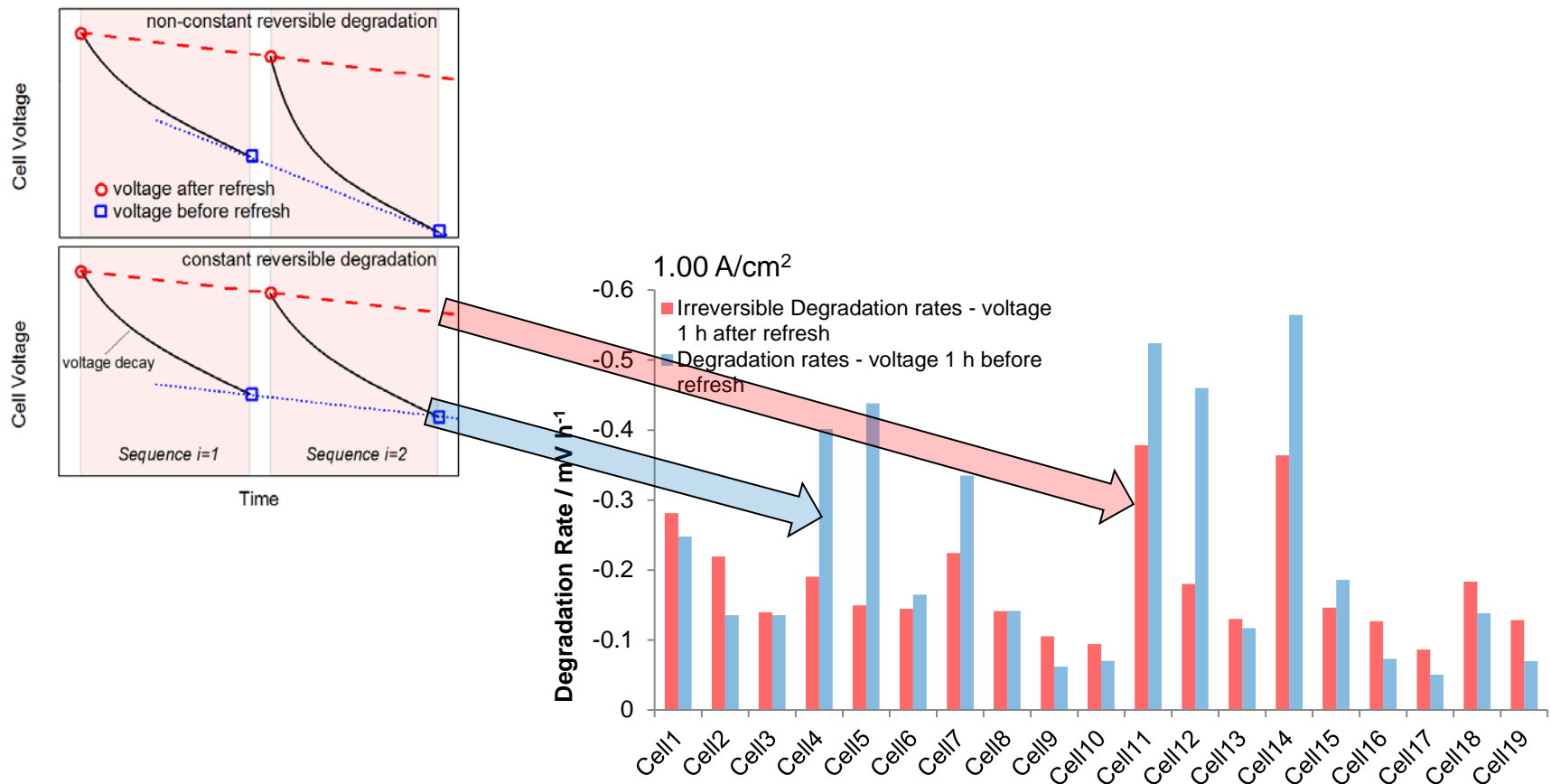
- Clear dependence of Cell Voltage on cathode Pt loading
- No dependence of Cell Voltage on anode Pt loading
- Onset of mass transport issues observed at cathode loading $\leq 0.2 \text{ mg/cm}^2$ and $j > 1 \text{ A/cm}^2$

Degradation Vs Pt-loading

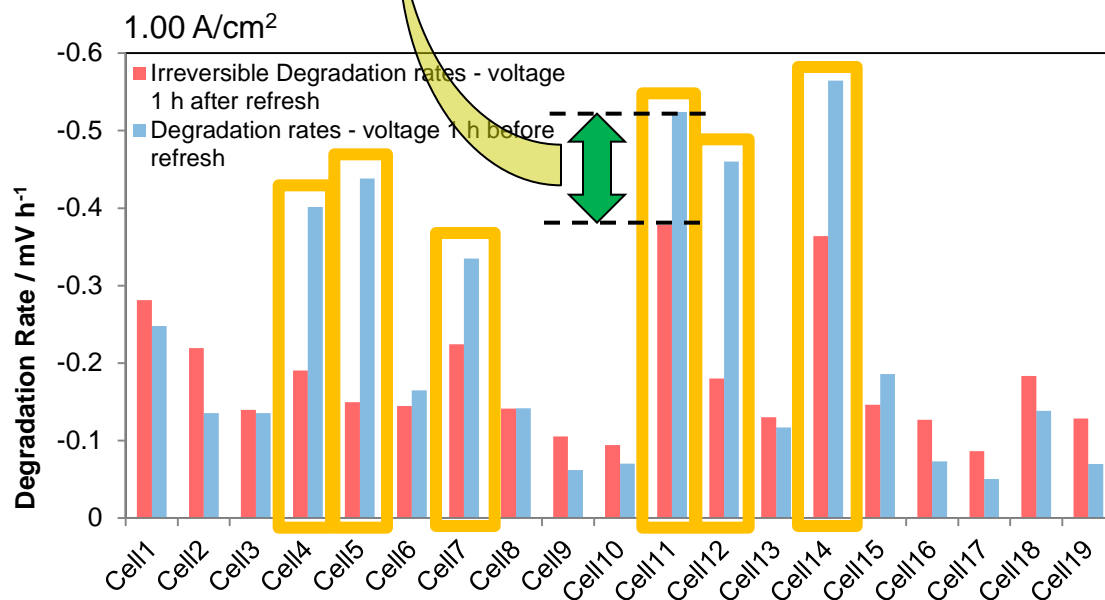
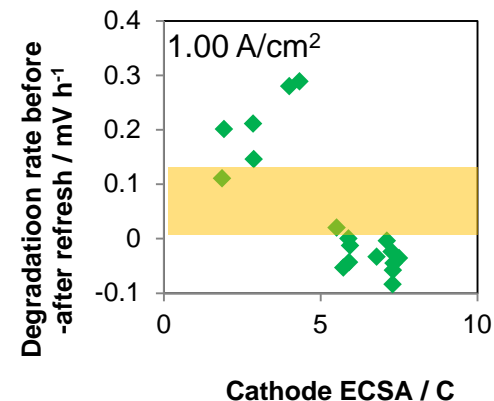
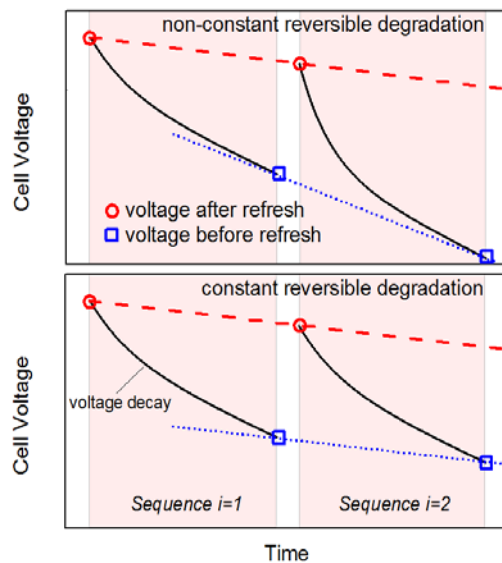
~500 h FC-DLC degradation test



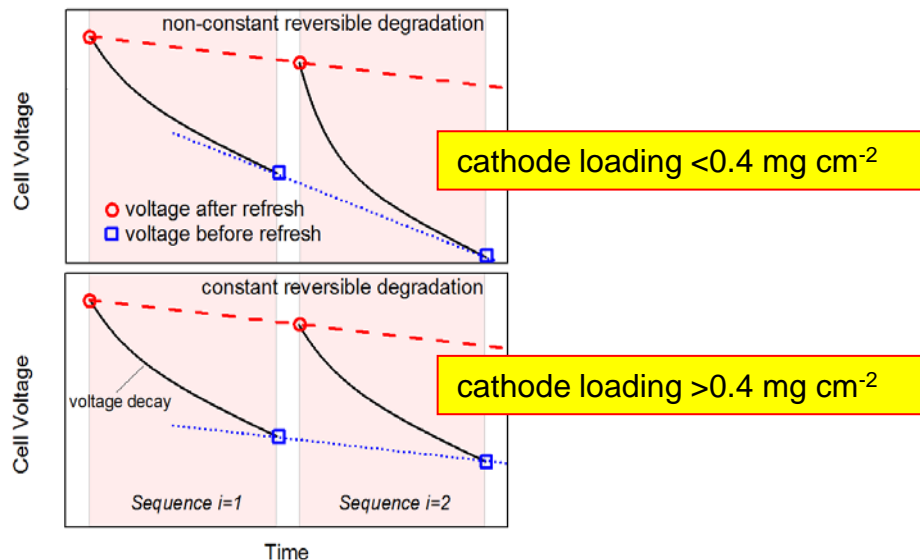
Degradation Vs Pt-loading: evaluation of rev. degradation



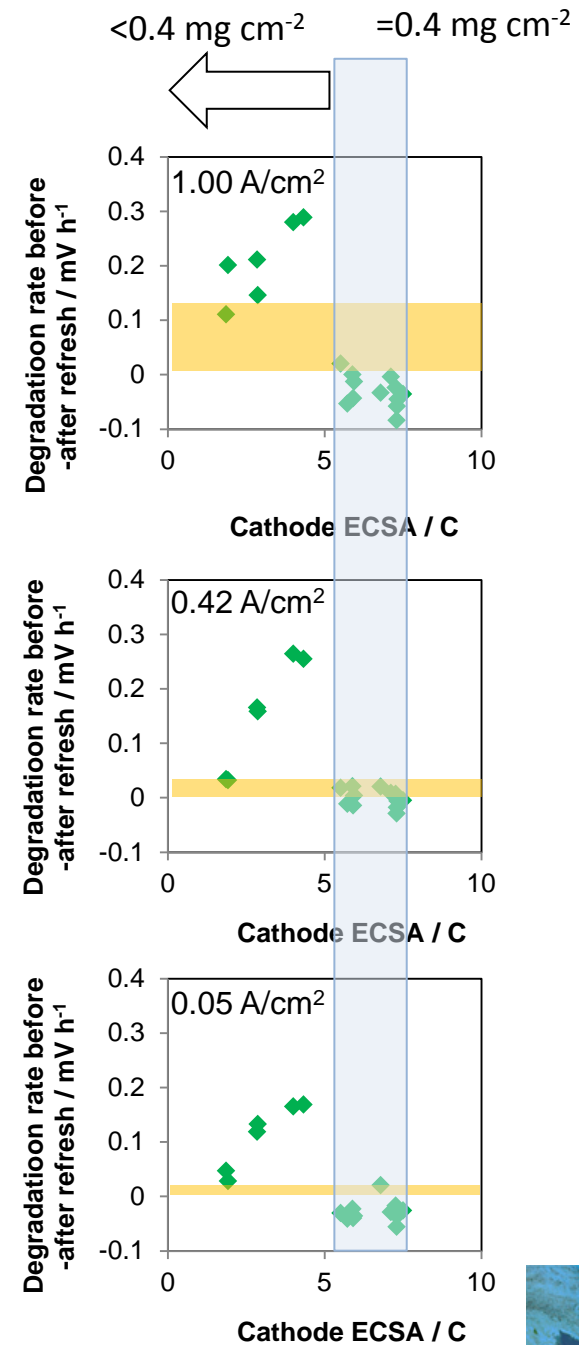
Degradation Vs Pt-loading: evaluation of rev. degradation



Degradation Vs Pt-loading: evaluation of rev. degradation

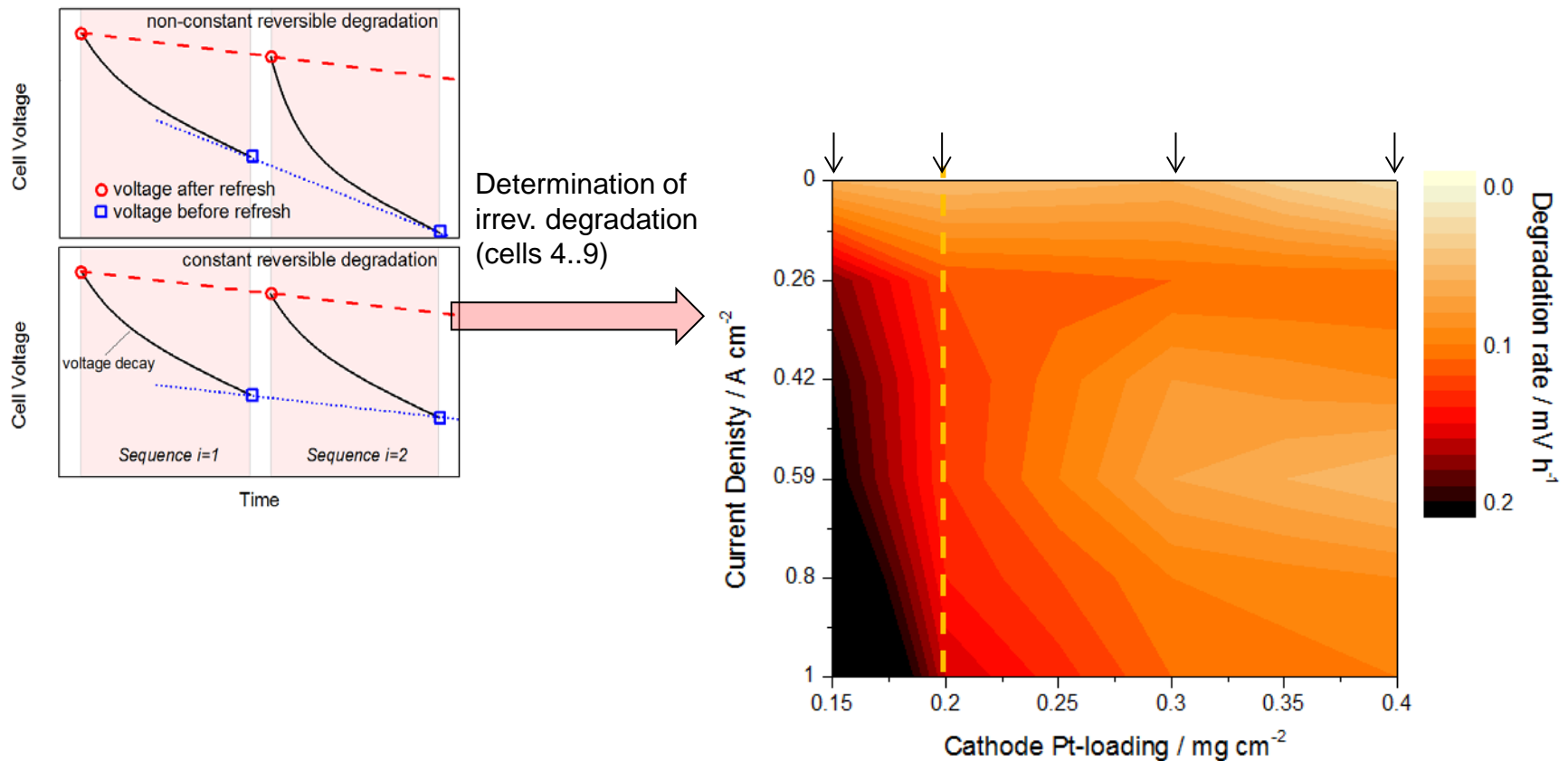


- MEAs with cathode loading $< 0.4 \text{ mg cm}^{-2}$ exhibit non-constant reversible degradation
- Effect strongest at high current density



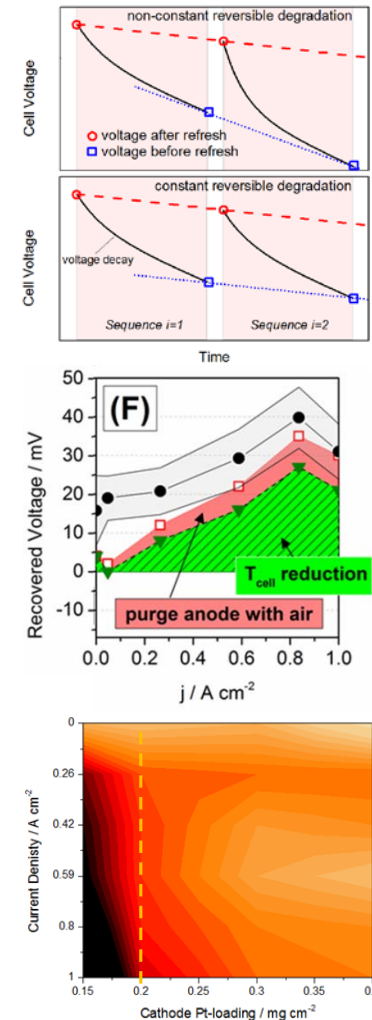
Degradation Vs Pt-loading: evaluation of irrev. degradation

Significant increase of irrev. degradation for cathode loading $< 0.2 \text{ mg/cm}^2$ and high loads



Summary

- Irreversible degradation rate: linear regression of voltage values after refresh
- Voltage recovery: water management, removal of anodic contaminants
- Degradation Vs Pt-loading:
 - accelerated rev. degradation for cathode loadings $< 0.4 \text{ mg cm}^{-2}$
 - increased irrev. degradation for cathode loading $< 0.2 \text{ mg cm}^{-2}$



Acknowledgements

Thank you for your attention.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for Fuel Cell and Hydrogen Joint Technology Initiative under Grant No. 621216 (**SecondAct**) and Grant n° 303452 (**Impact**).

